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SYNTHESIS OF ZnS WHISKERS

by

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SYNTHESIS OF ZNS WHISKERS

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ABSTRACT:

One approach to improving the mechanical performance of a material is to form a self-similar whisker reinforced composite. This is the approach we are developing for ZnS optical windows; however, it has necessitated the development of synthesis methods for ZnS whiskers. Recently, we reported an organometallic route to ZnS whiskers [1-2]. Here we report yet another synthesis route. This non-organic route involves the surface reaction of metallic zinc foil or wire in a flowing atmosphere of H_2S (T_{max}=350°C). The ZnS whiskers created at the zinc surface were characterized using SEM, TEM, SIMS, and x-ray diffraction. After an 8 hour 350°C thermal treatment, the whiskers were ZnS averaging 19.2 μm in length, aspect ratio 27. The whiskers are single crystal in nature, and appear to evolve through an oxide layer at the surface of the zinc substrate. Thermochemical analysis of the reaction was performed to establish the relative stability of ZnS and various oxide and sulfates, and these confirmed the experimental data. These calculations describe the effects of temperature and gas phase composition upon the thermochemical stability of ZnS and other solid phase reaction products. The calculations are exceedingly useful for determining and controlling the process parameters and for the evaluation of the experimentally observed products.

1. INTRODUCTION

Advanced optical window materials for 8-12 μm have attracted considerable investigation during the last decade [3-4]. Because the windows will be subjected to harsh environmental conditions, such as rain erosion and thermal shock due to aerodynamic heating, survey work has been conducted to identify materials possessing optimum optical, thermal and mechanical properties [5-6]. For applications up to several hundred degrees centigrade, ZnS is the best optical material presently available [7], but the mechanical performance of these windows may be compromised using ZnS. Thus, investigations have been conducted to develop new materials such as the rare earth ternary sulfides [8-9]; here, the optical performance is improved through a compromise in mechanical and thermal performance. The approach in our laboratory is to explore methods of improving the

mechanical properties of ZnS infrared optical materials. Rather than developing new families of materials, here the objective is to develop a self-similar ZnS/ZnS whisker reinforced composite. The key issue is the synthesis of materials which can be processed to create a uniform homogeneous ceramic whose mechanical performance is enhanced without sacrifice of the optical transmission. A similar approach has been demonstrated by E. Fitzer and co-workers for Al_2O_3/Al_2O_3 fiber reinforced composites in which a three-fold increase in fracture toughness from 4 $MNm^{1/2}$ for polycrystalline Al_2O_3 to 12 $MNm^{1/2}$ for fine-grained Al_2O_3 containing 40% Al_2O_3 fibers was shown [11].

To fabricate infrared transmitting ZnS/ ZnS composites requires the development of high aspect ratio (>10), micrometer sized ZnS whiskers. Unfortunately, the common methods for synthesis of ZnS do not achieve this requirement. The two classical routes are vapor transport [12-13] and chemical transport [14-16]. In the vapor transport process, high purity polycrystalline ZnS is sublimed at 1200°C and recondensed in a gradient temperature furnace. The resulting crystals take on a number of irregular morphologies. Similarly, the chemical transport process, involving ZnS crystal growth from ZnS vapor in the presence of iodine or HCl, and thus operating at lower vaporization temperatures, 850-900°C, results in large millimeter ZnS single crystals. Clearly, these high temperature processes do not yield the growth conditions where uniform, sub-micron ZnS whiskers can be synthesized. Thus, two alternative routes to greater ZnS whisker morphology control have been developed in our laboratory. The first, the organometallic route, involves a thiolysis-condensation solution reaction between the pentameric $[(C_2H_5)Zn(SBu^t)]_5$ precursor and H_2S, followed by a thermal treatment (T_{max}= 500°C) under flowing H_2S. The results have previously been reported [1-2]. The second route, the metal sulfidation route, involves ZnS whisker growth from metallic zinc surfaces which are thermally treated under flowing H_2S. It is this later synthesis route which we herein report.

2. EXPERIMENTAL

2.1 ZnS Whisker Synthesis

Figure 1 illustrates the schematic experimental setup employed in processing single crystal ZnS whiskers from metallic zinc and H_2S gas. High purity zinc (>5N, foil, sheet or powder, Electronic Space Products) was placed in a Pyrex boat. The boat was centered within a fused quartz tube furnace under a flowing atmosphere of H_2S. A constant H_2S flow, ranging (70-100cc/min) was maintained during the complete thermal cycle (see Table

1). Upon cooling to room temperature, the H_2S flow was discontinued, and the resulting products were removed from the reaction tube for characterization.

The reaction products were analyzed by x-ray powder diffraction, secondary electron microscopy (SEM), transmission electron microscopy (TEM), and secondary ion mass spectroscopy (SIMS). X-ray powder diffraction, in addition to selected area electron diffraction, were used to verify composition and phase. Morphological characterization was performed using the SEM and the TEM techniques. SIMS was used to monitor the elemental composition of the surface reaction layer as a function of processing temperature.

2.2 Thermochemical Calculations

Chemical equilibrium calculations were conducted to determine the extent to which the stability of ZnS is sensitive to the gas composition and temperature of the system. The calculations were performed using the SOLGASMIX computer program written by Eriksson [17-18]. This program is based on the approach developed by White et al. [19] which minimizes the total free energy of the system according to equation 1:

$$G/RT = \sum x[(g/RT) + \ln(P) + \ln(x/X)]_{gases} + \sum x[(g/RT) + \ln(x/X)]_{liquids} + \sum x(g/RT)_{solids} \quad (1)$$

where G is the total free energy, x is moles iterated by the computer, P is the partial pressure of the gaseous species, g is the free energy of formation for each species, and x/X is the mole fraction of solution species.

Two primary elemental systems, an oxygen free and an oxygen containing Zn-S-H system, were considered. Data sets comprised of the ΔH_f's (joules/mole) and ΔS_f's (joules/k-mole) were compiled from JANAF [20] and a number of other sources [21-24]. Tables II and III list the various solids, liquids and gaseous species included in the equilibrium calculations along with their thermodynamic data obtained at 323 K. These data along with the temperature, total pressure, and input concentrations of each individual element in the system were used to calculate the equilibrium composition and activities of the gas, liquid, and solid species.

The equilibrium assemblage of gaseous and solid reaction products was determined as a function of temperature and increasing H_2S and O_2 concentrations; the total pressure was maintained at 1 atm. The mole fractions and partial pressures of oxygen containing species were calculated to establish the role of oxide layers on the metallic zinc reactant.

3. RESULTS

3.1 Morphology

After an 8 hour thermal treatment at 350°C, whiskers are observed on the reacted surface of metallic zinc (Figure 2). In an effort to monitor the growth process, the reaction was followed as a function of the thermal treatment conditions. Figure 3 shows the SEM micrograph of the reaction products created at the surfaces as a function of treatment temperature from 25-200°C. After 0.5 hours at 150°C, the as received zinc metal surface (Figure 3A) develops a granular surface reaction product (Figure 3B). After 0.5 hours at 200°C, a distinct surface layer is no longer evident and a smooth surface results (Figure 3C). With further treatment, nucleation sites develop at the surface and whisker growth is observed (Figure 4).

The rate of whisker growth was studied as a function of time at the maximum 350°C reaction temperature (Figure 5). In order to indicate the control of whisker dimensions which might be achieved as a function of process control, the average whisker lengths are plotted as a function of time in Figure 6.

X-ray powder diffraction patterns were collected as a function of thermal treatment and are presented in Figure 7. The results verify conversion from Zn to ZnS on the basis of d-spacings. In no case were oxide lines observed. TEM analysis further verified that the whiskers were indeed single crystal products (Figure 8). In addition, TEM selected area diffraction verified that the single crystal whiskers were ZnS (Wurtzite).

3.2 Surface Analysis

Although oxides were not detected in the powder x-ray diffraction, surface analyses revealed the existence and transformation of an oxide layer, approximately 100 nm thick, on the zinc foil surface. During the initial stages of whisker growth, this layer evolved into a duplex structure. The in-depth profiles in Figure 9 reveal the progressive loss of oxygen due to an apparently kinetic limited penetration of sulfur into the oxide layer. For the 300°C treatment, the oxide layer was no longer evident.

3.3 Thermochemcal Calculations

The thermochemical calculations verified that ZnS was the stable equilibrium product in the Zn-S-H system for temperatures ranging 25-500°C. The calculations predict ZnS

(Sphalerite) and no other solid phase reaction products. The calculations ere carried out under conditions of excess zinc, and the predominate gaseous species were H_2 and Zn.

Because the oxide layer was observed by SIMS, the introduction of oxygen into the calculations was of interest. In the Zn-S-O-H system, a range of oxygen-to-sulfur concentrations between 0.0 and 1.5 were used in the 350°C calculations. Under these conditions, no oxides or sulfates were found to be stable reaction products. The oxygen existed primarily in the form of OH.

4. DISCUSSION

The experimental results of this study are consistent with the thermochemical predictions; namely, ZnS is the equilibrium solid phase even in the presence of an oxide surface layer. Clearly, the overall chemical reaction is simply:

$$Zn\,(s) + H_2S\,(g) \text{ -----> } ZnS\,(s) + H_2\,(g) \qquad (2)$$

The growth mechanism is not yet known, but the initial reduction of oxides by H_2S may play a role in the nucleation step.

SIMS analyses confirm the transition of a zinc oxide surface layer to a sulfur rich zone prior to the appearance of ZnS whiskers. Indeed, up to the 200°C, a duplex reaction product layer is detected.The in-depth profiles suggest the penetration of sulfur into the oxidized surface, although the roughness of these surfaces preclude any quantitative verification of a diffusion reaction. Surface reaction studies on smooth Zn and ZnO single crystals will be required to verify these suggestions. Nevertheless, once the oxide layer has been consumed (as shown in the SIMS profiles), the creation of ZnS- and at temperatures > 200°C ZnS whiskers- are observed (as shown in the XRD and SEM results).

The TEM studies verified the single crystalline nature of the whiskers. The surfaces of the whiskers appear smooth and defect free, and this implies that the whiskers can adequately reinforce the polycrystalline ZnS ceramic matrix.

5. CONCLUSIONS

In this study, it has been demonstrated that single crystal ZnS (Wurtzite) can be synthesized from metallic zinc and H_2S at low temperatures (350°C). In contrast to the high temperature vapor routes where large crystals with irregular shapes and sizes are created, the low route reported here yields highly reproducible micrometer sized single

crystal ZnS whiskers. Indeed, the resulting whisker growth reaction has been found to be dependent on the period of time at maximum processing temperatures. Thus, these results indicate that controlled whisker size distributions, from < 1.0 μm to 20.0 μm, may potentially be processed on a large scale. The ability to control size is critical because it must be optimized to enhance fracture resistance and minimize scattering losses. Most significant is that this is the size range of interest for ZnS whiskers to be used in optical composites. Efforts are currently in progress to fabricate ZnS/ ZnS whisker reinforced composites and in turn to evaluate the effect of whisker morphology upon the mechanical and optical properties of the composites.

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TABLE I. THERMAL CYCLE

TEMPERATURE [°C]	TIME [Minutes]
25-150	45
150-200	30
200-200	30
200-350	30
350-350	x

TABLE II. THERMODYNAMIC DATA FOR Zn-S-H SYSTEM

	ΔH_f (Joules/Mole)	ΔS_f(Joules/KMole)
Gas Species		
Ar	0.	0.0
H	218637.	-51.22
HS	138794.	-113.05
H_2	0.	0.0
H_2S	-24549.	-31.99
S	274732.	-129.94
S_2	122718.	-148.37
S_3	132621.	-149.76
S_4	134459.	-152.34
S_5	95756.	-112.26
S_6	85991.	-119.60
S_7	95393.	-134.99
S_8	79803.	-119.6
Zn	129902.	-117.79
ZnH	227610.	-89.38
Liquid Species		
S	0.	0.0
Zn	6519.	-9.08
Solid Species		
S	-2212.	5.75
Zn	0.	0.0
ZnS (Sphalerite)	-205800.	23.16
ZnS (Wurtzite)	-192040.	15.54

TABLE III. THERMODYNAMIC DATA FOR Zn-S-O-H SYSTEM

	ΔH_f (Joules/Mole)	ΔS_f (Joules/K-Mole)
Gas Species		
Ar	0.	0.0
H	218637.	-51.22
HO	39029.	-1592
HO_2	1260.	43.79
HS	138794.	-113.05
H_2	0.	0.0
H_2O	-242846.	47.36
H_2O_2	-137417.	106.65
H_2S	-24549.	-31.99
O	249868.	-60.50
OS	1998.	-79.27
OS_2	-57945.	-128.80
O_2	0.	0.0
SO_2	-300257.	-1.79
SO_3	-399412.	92.93
S	274732.	-129.94
S_2	122718.	-148.37
S_3	132621.	-149.76
S_4	134459.	-152.34
S_5	95756.	-112.26
S_6	85991.	-119.60
S_7	95393.	-134.99
S_8	79803.	-119.6
Zn	129902.	-117.79
ZnH	227610.	-89.38

	ΔH_f (Joules/Mole)	ΔS_f (Joules/K-Mole)
Liquid Species		
H_2O	-282591.	153.96
$SO_3 \cdot 2\,H_2O$	-1123193.	581.40
$SO_3 \cdot 3\,H_2O$	-1421376.	746.23
$SO_3 \cdot 4\,H_2O$	-1713566.	907.24
$SO_3 \cdot 5\,H_2O$	-2002190.	1065.0
$SO_3 \cdot 7.5\,H_2O$	-2717228.	1454.5
S	0.	0.0
Zn	6519.	-9.08
Solid Species		
$ZnSO_4$	-982499.	379.78
$ZnSO_4 \cdot H_2O$	-1299500.	526.93
$ZnSO_4 \cdot 6\,H_2O$	-2775200.	1402.8
$ZnSO_4 \cdot 7\,H_2O$	-3075700.	1596.0
S	-2212.	5.75
Zn	0.	0.0
ZnO	-348320.	92.63
$Zn(OH)_2$	-642240.	284.45
ZnS (Sphalerite)	-205800.	23.16
ZnS (Wurtzite)	-192040.	15.54

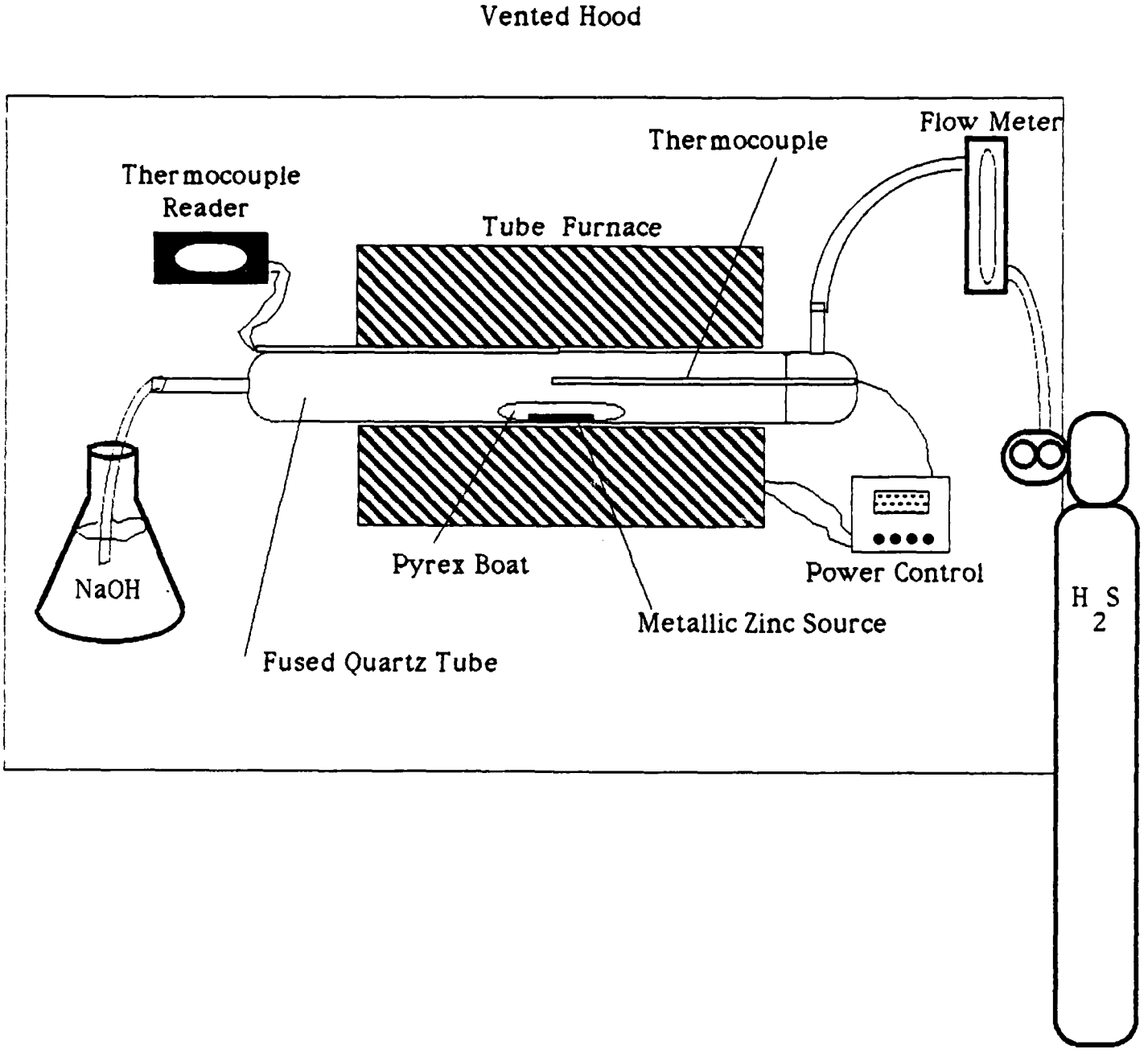

Figure 1. Schematic Representation of Experimental Set Up

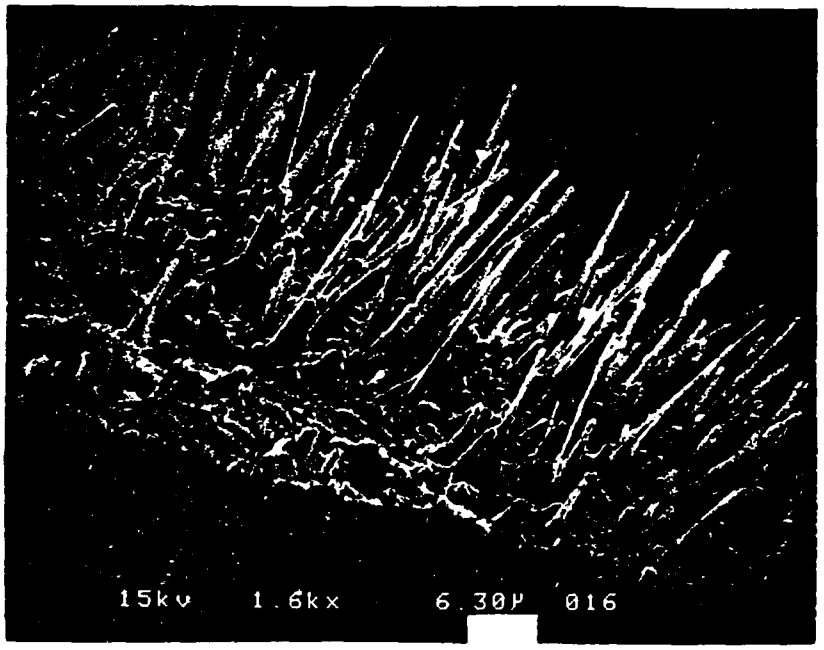

Figure 2. ZnS Single Crystal Whiskers on Metallic Zinc Surface
(350°C, 8.0 Hours, 75 cc/min H_2S)

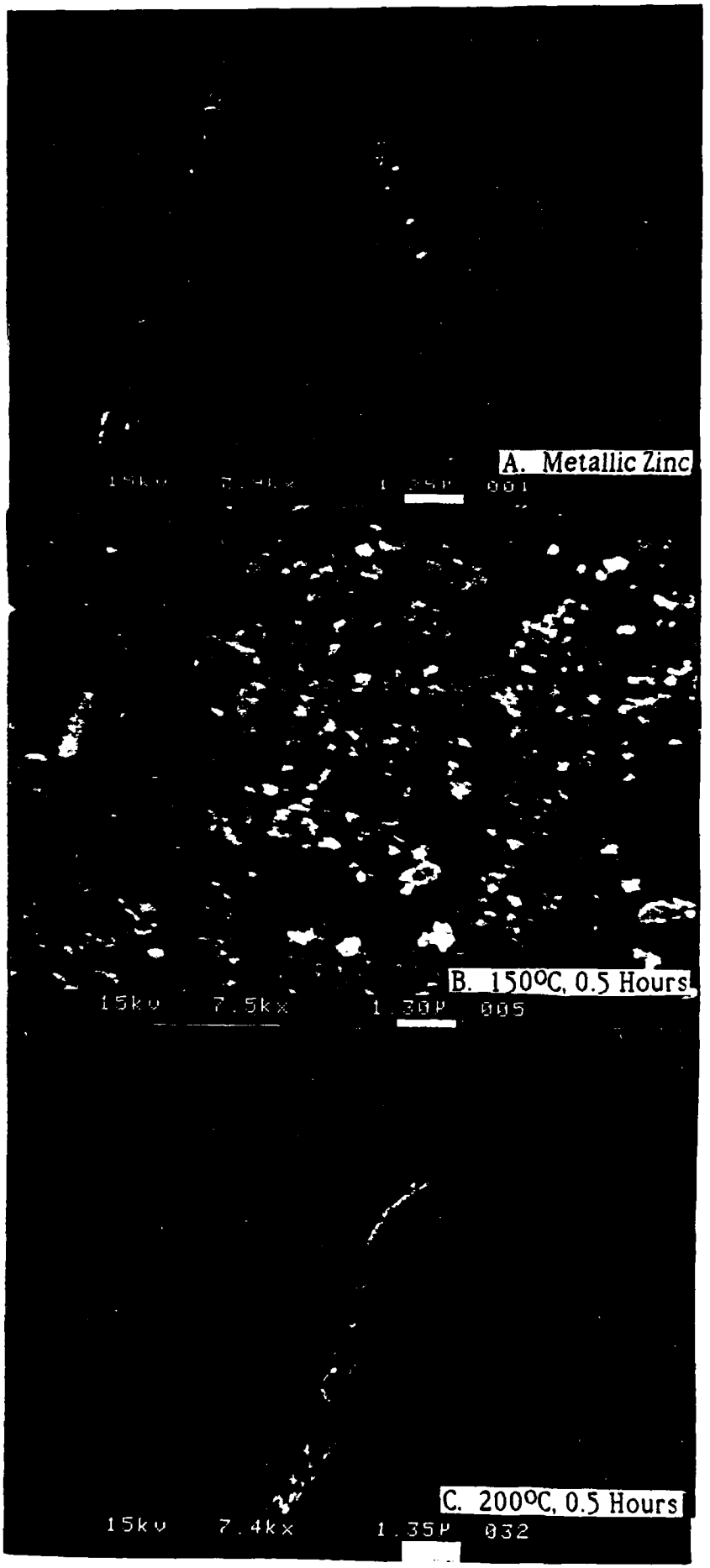

Figure 3. Metallic Zinc/ H_2S Reaction Product Surfaces

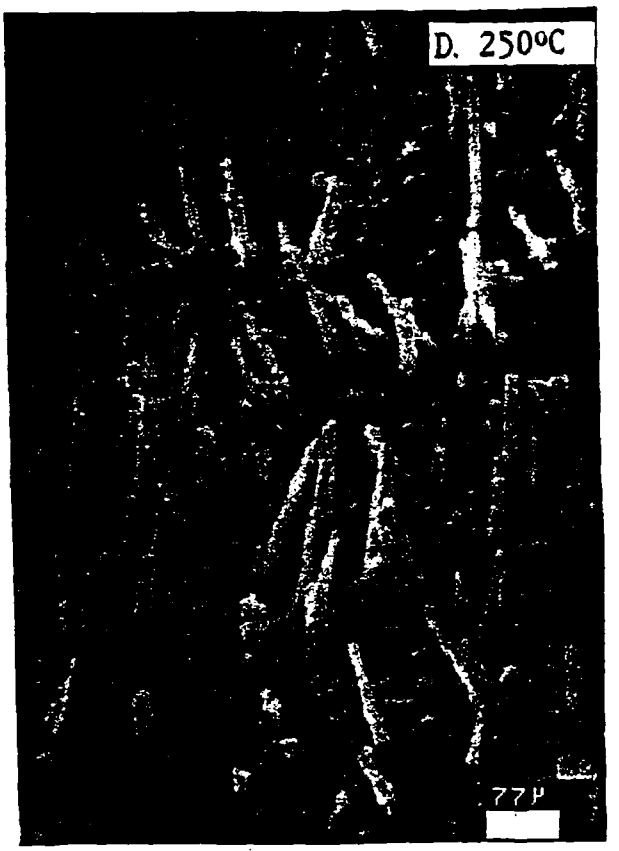

Figure 4. ZnS Nucleation Surface Sites and Whiskers
(250°C, 0.5 Hours, 75 cc/min H_2S)

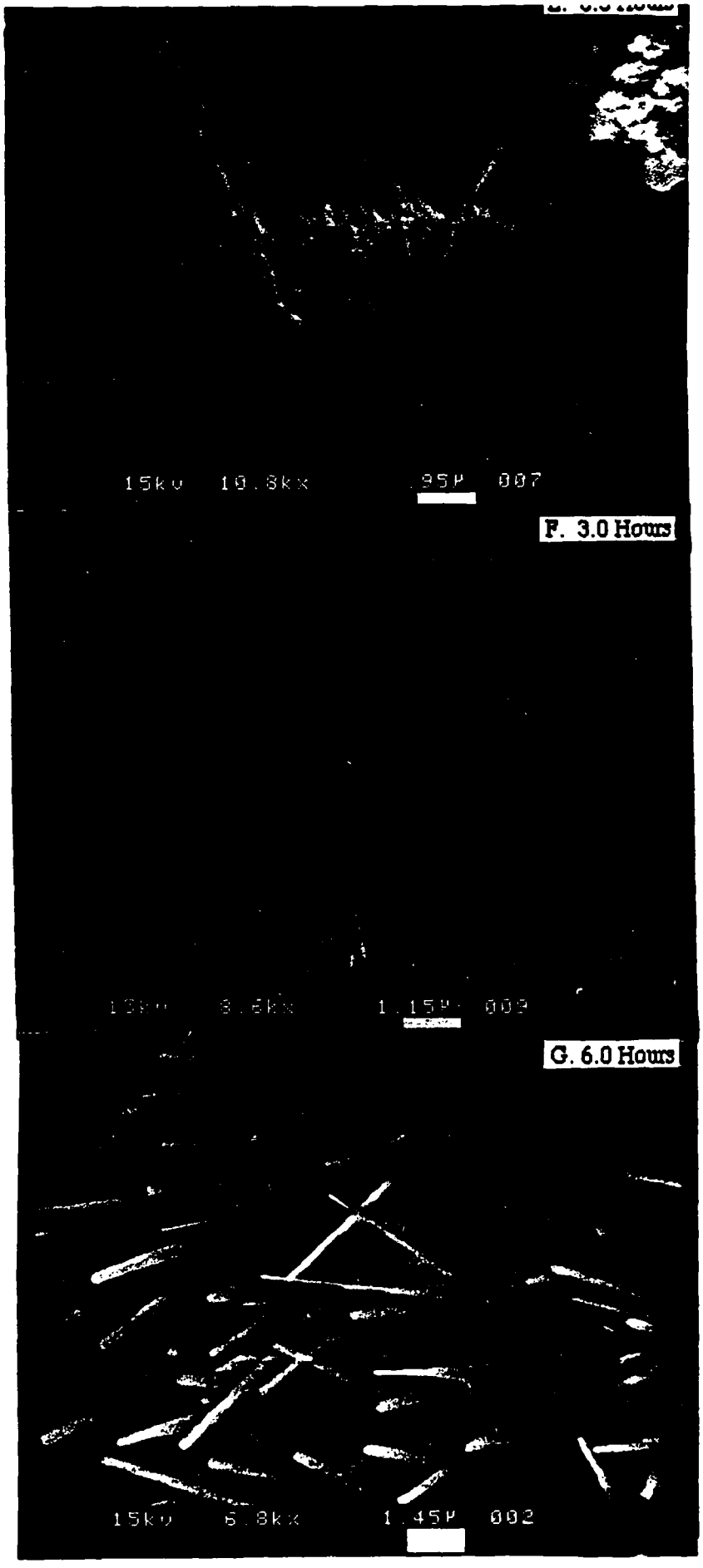

Figure 5. SEM Analysis of ZnS Whisker Growth As a Function of Reaction Time at 350°C

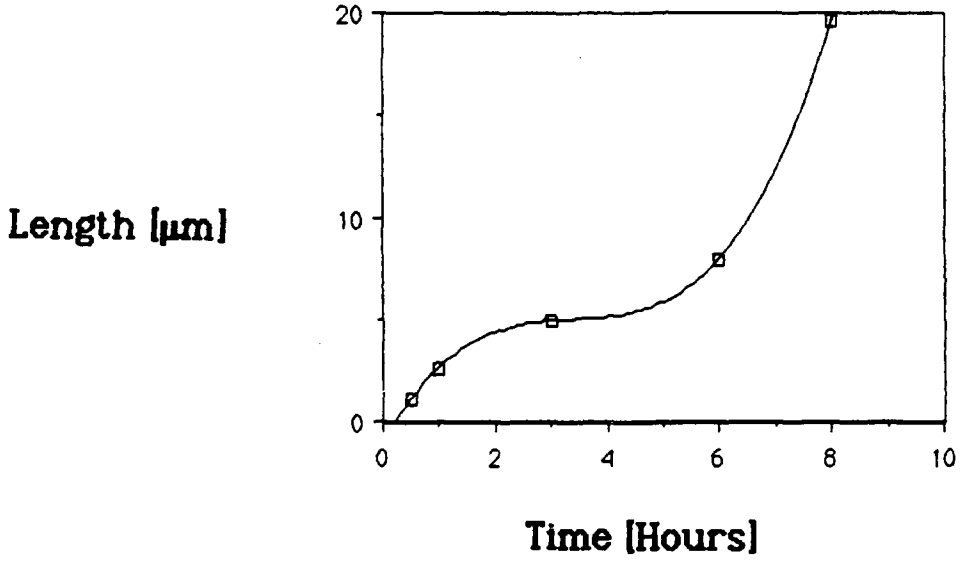

Figure 6. ZnS Whisker Length As a Function of Reaction Time at 350°C

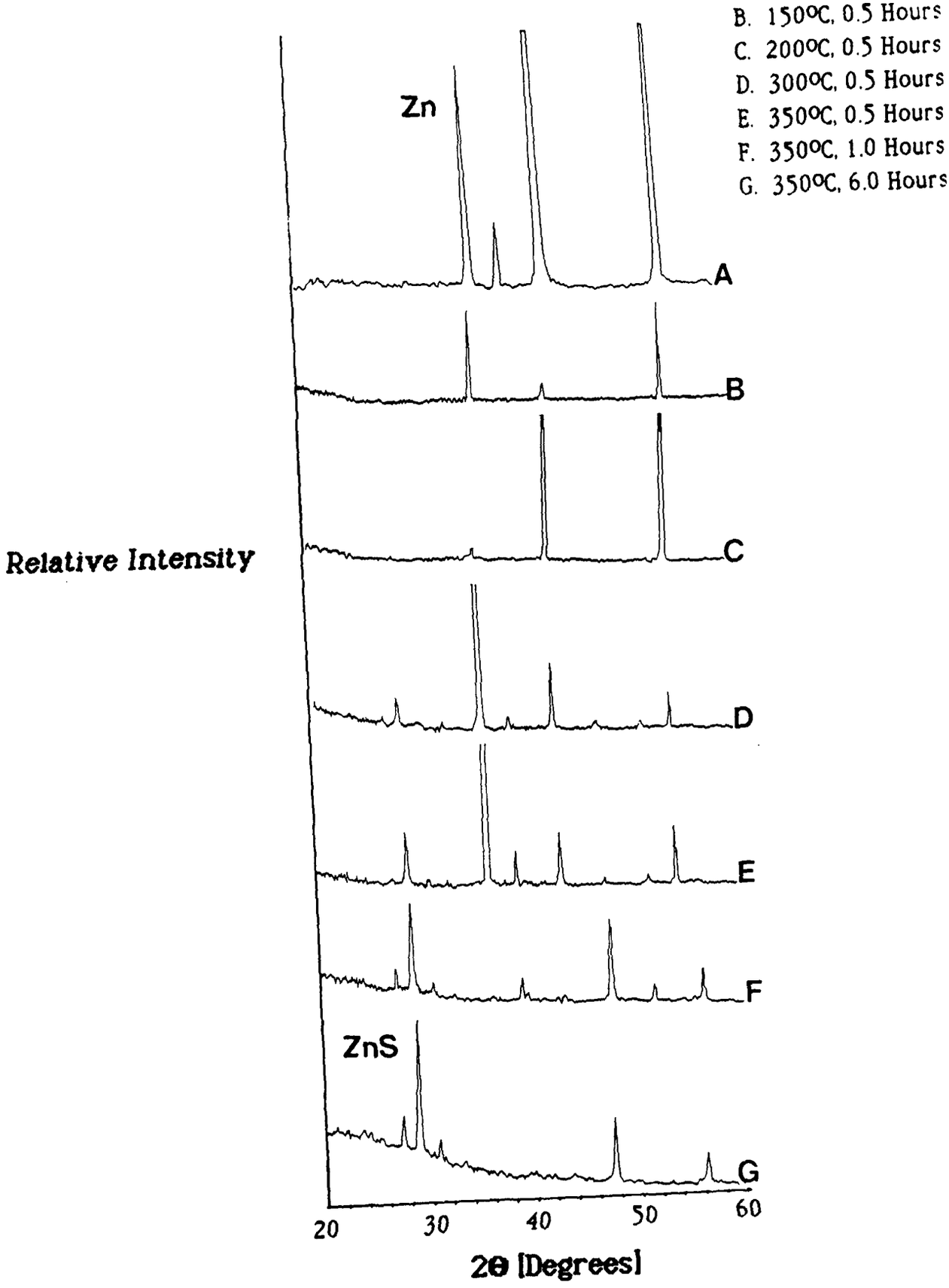

Figure 7. X-ray Powder Diffraction of H_2S Thermally Treated Zinc Products

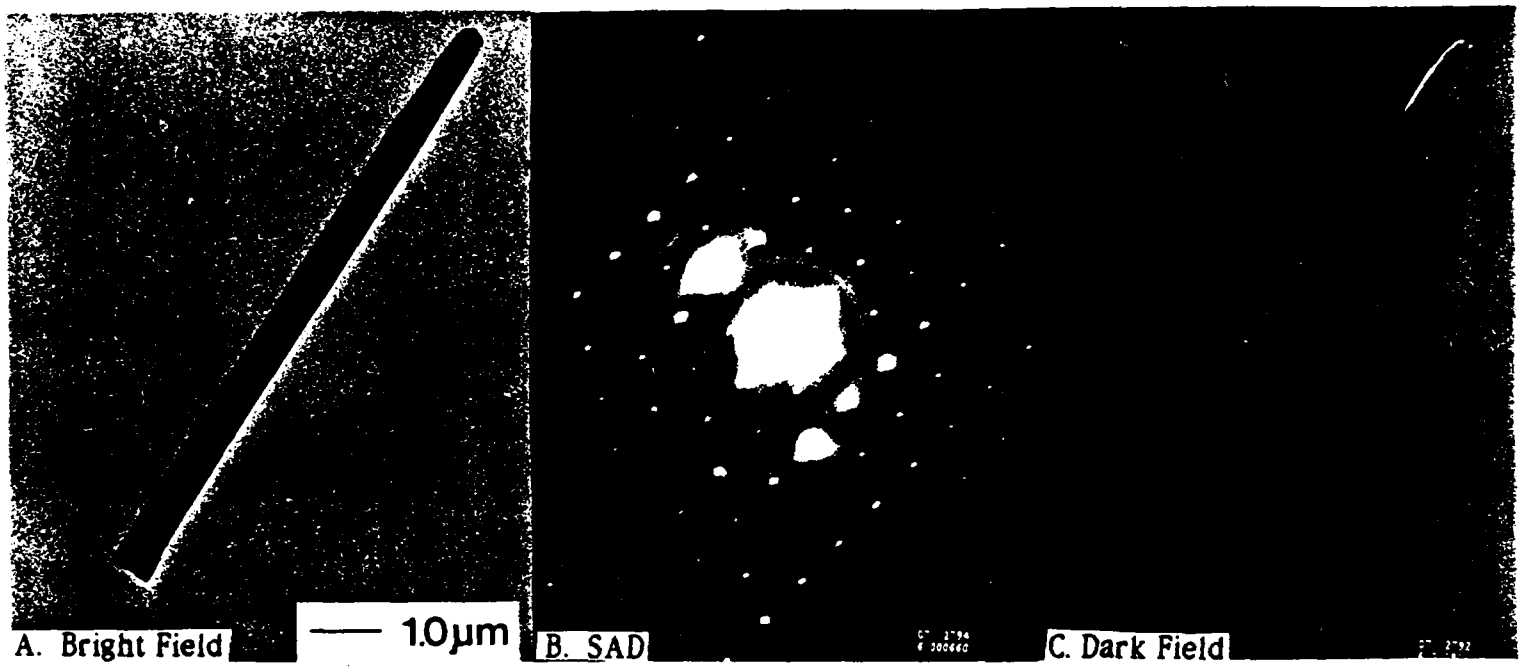

Figure 8. TEM Micrograph of ZnS Single Crystal Whisker

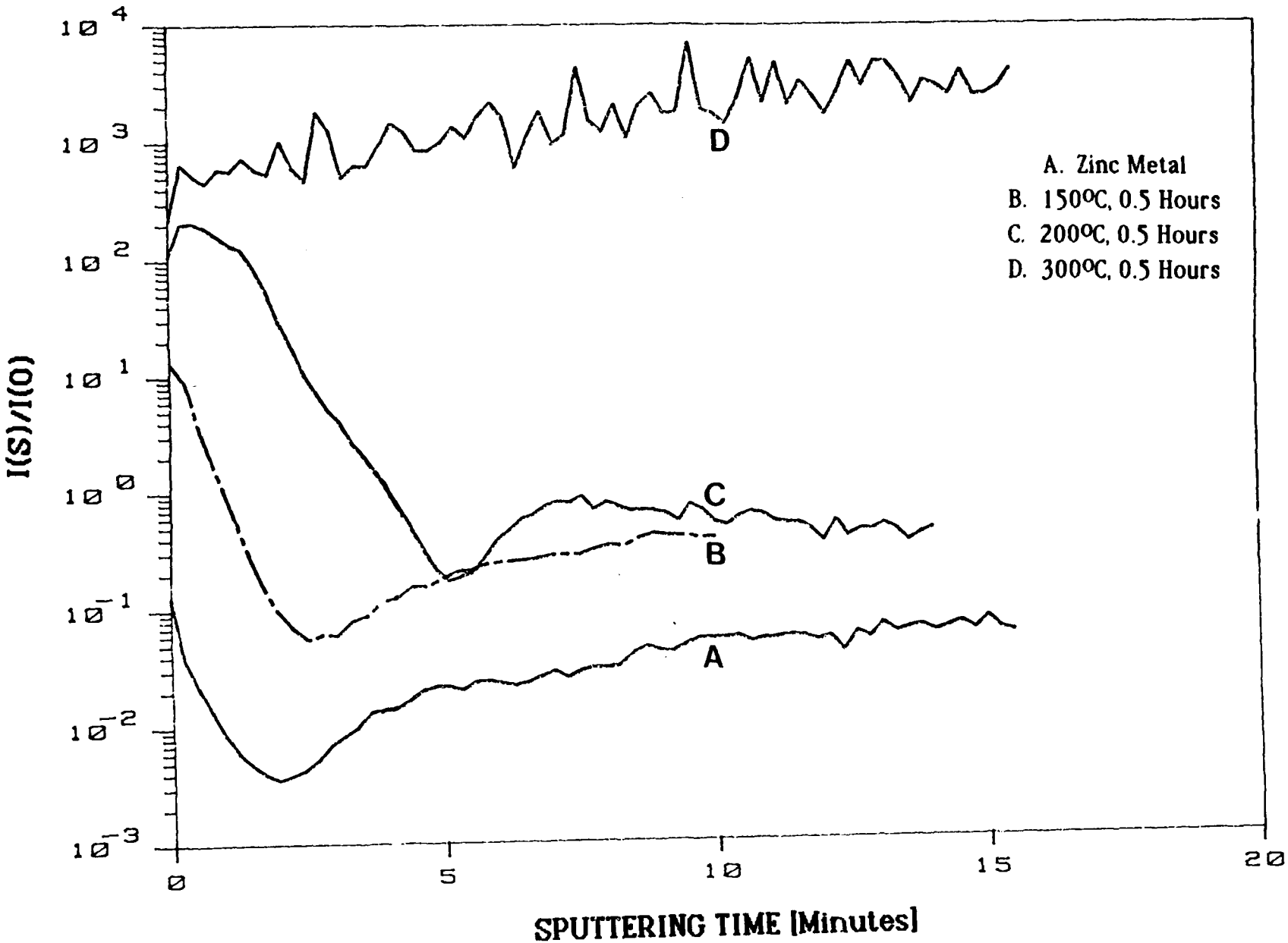

Figure 9. SIMS Analysis: Relative Intensity of Sulfur to Oxygen Signal As a Function of Sputtering Time and Thermal Treatment

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